

# **EFFECT OF DIFFERENT SHEAR RATE ON PERFORMANCE OF PES ASYMMETRIC MEMBRANE FOR GAS SEPARATION**

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## DECLARATION

I declare that this thesis entitled “Effect of Different Shear Rate on Performance of PES Asymmetric Membrane for Gas Separation” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....

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Date : 20 November 2006

Dedicated to my beloved father, mother, and family.....

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## **ABSTRACT**

Membrane based gas separation process technology has been recognized as one of the most efficient and advanced unit operation for gas separation. The main problem in membrane gas separation is the trade off between permeability and selectivity. The membrane that provide high permeability offered low selectivity and vice versa. Therefore in this study, a high performance Polyethersulfone (PES) flat sheet asymmetric membrane will be fabricated based on high of both permeability and selectivity. The main objectives of this study are to illustrate the effect of shear rate on asymmetric membrane structure and gas separation performance. The membranes are produced by a simple dry/wet phase inversion technique using a conventional method. By using several membrane with different shear rate, the membranes then been installed to the gas permeation rig and to be tested by natural gas which are oxygen and nitrogen. Then, the permeability and selectivity can be calculated. The membrane with the optimum performance was chosen for further membrane fabrication.

## **ABSTRAK**

Membran yang menggunakan teknologi proses pengasingan gas telah dikenalpasti sebagai salah satu unit operasi yang paling berkesan dan maju. Masalah utama dalam proses ini ialah dalam mengenalpasti antara pemisahan dan pemilihan gas tersebut. Membran yang menghasilkan kadar pemisahan yang tinggi akan mempunyai kadar pemilihan yang rendah dan begitulah sebaliknya. Oleh itu dalam kajian ini, suatu membran Polyethersulfone (PES) yang rata, leper dan asimetrik dan berprestasi tinggi akan dibuat berdasarkan kadar pemilihan dan pemisahan yang tinggi. Tujuan kajian ini adalah untuk mengkaji kesan kadar pemotongan ke atas struktur membran asimetrik dan prestasi pengasingan gas. Membran tersebut dibuat dengan proses pemisahan fasa kering/basah dengan menggunakan kaedah konvensional. Dengan menggunakan membran yang mempunyai perbezaan kadar pemotongan, membran kemudian dipasang kepada mesin pemisahan gas untuk diuji dengan gas tulen iaitu oksigen dan nitrogen. Kemudian, kadar pemisahan dan pemilihan dikira. Membran yang mempunyai prestasi yg optimum dipilih bagi pembentukan membrane seterusnya.

## **TABLE OF CONTENT**

<b>CHAPTER</b>	<b>TITLE</b>	<b>PAGE</b>
	ABSTRACT	ii
	TABLE OF CONTENT	iii
	LIST OF TABLE	vii
	LIST OF FIGURES	viii
<b>1</b>	<b>INTRODUCTION</b>	
	1.1 Problem Statement	2
	1.2 Objectives of the Research	3
	1.3 Scope of the Research	3
<b>2</b>	<b>LITERATURE REVIEW</b>	
	2.1 History of Membrane Based Separation	4
	2.2 Overview of Membrane	6
	2.3 The Advantages of Membranes Technologies	7
	2.4 Classification of Membranes	8
	2.4.1 Symmetric Membranes	9
	2.4.2 Asymmetric membranes	10
	2.5 Application of Membrane Separation Process	12
	2.6 Membrane Formation	14
	2.7 Fundamental of Gas Separation	17
	2.8 Terminology of Gases	18

2.9	Gas Permeation Experiment	20
2.10	Current Status of Gas Separation Membrane	21
2.11	Factor Affecting Gas Permeation in Membrane	22
2.12	Effect of Shear Rate	23

### 3

## METHADODOLOGY

3.1	Materials	
3.1.1	Polyethersulfone (PES)	25
3.1.2	Methyl -2-Pyrrolidone (NMP)	26
3.2	Physical Properties of Gases	26
3.3	Preparation of Flat Sheet Asymmetric Membranes	27
3.4	Dope Formulation	
3.4.1	Preparation of Homogenous Dope Solution	28
3.5	Research Design	
3.5.1	Membrane Casting	29
3.6	Membrane Testing	29
3.7	Gas Permeation Rig	30

### 4

## RESULT AND DISCUSSION

4.1	Effect of Shear Rate on Membrane Separation Performance	32
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**CONCLUSION AND RECOMMENDATION**

5.1 Conclusion 39

5.2 Recommendation 40

**REFERENCES** 41

**APPENDICES**

**LIST OF TABLES**

<b>TABLE</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Milestones in the development of membrane based separation	5
2.2	Applications of membrane separation process	11
2.3	Lennard-Jones collision diameter of some gas molecules	17
2.4	Principal Gas Separation Markets, Producers and Membrane Systems	21
3.1	Physical properties of oxygen and nitrogen	25
4.1	Result of membrane performance of 4 s shear rate with different pressure	33
4.2	Result of membrane performance of 8 s shear rate with different pressure	34
4.3	Result of membrane performance of 12 s shear rate with different pressure	35

## LIST OF FIGURES

FIGURE	TITLE	PAGE
2.1	Membrane separation process	7
2.2	Classification of membrane	8
2.3	Phase inversion techniques	13
2.4	Schematic representation of phase inversion processes	15
2.5	Membrane gas separation	16
2.6	Terminology of gases	18
2.7	Schematic representation of main mechanism of membrane-based gas separation	18
3.1	Chemical bonding of polyethersulfone	24
3.2	Chemical bonding of NMP	25
3.3	Main step in preparing flat sheet asymmetric membranes	26
3.4	Steps in membrane testing	29
3.5	Schematic of gas permeation cell	30
4.1	Permeability of N <sub>2</sub> and O <sub>2</sub> with the different shear rate on 10 psia pressure	36
4.2	Selectivity of O <sub>2</sub> / N <sub>2</sub> with the different shear rate on 10 psia pressure	37
4.3	Selectivity versus shear rate with different pressure	38

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Gas Separation Membranes**

Gas separation by selective permeation through polymer membranes is one of the fastest growing branches of the separation technology. Gas separation membrane systems have received a lot of attention from both industry and academia. This is because there is a belief that membrane separation processes may offer more capital and energy efficiency when compared to the conventional separation processes in some application. In order to accomplish this objective, membrane materials with superior permeability and selectivity and advanced fabrication technologies to yield hollow fibers with an ultra-thin dense selective layer are the primary focuses for most membrane scientists in the last two decades.

Most of the membrane expert have been investigating and synthesizing new polymers that are able to exhibit both higher gas permeabilities and selectivities since the past 40 years. Presently, the structure, pressure-normalized flux and selectivity of the membrane polymer have become the focus of the studies among researchers. In addition, they are aiming for defect-free ultrathin dense selective layer membrane materials. Significant progresses have been made in the membrane materials, dope preparation, fabrication technology and fundamental understanding of membrane formation.

The effect of shear rate has been observed in the separation performance of ultrafiltration, reverse osmosis and gas separation membranes. The selectivity increased with increasing dope extrusion rate in hollow fiber spinning while the gas permeation rate reduced. The relative selectivities also increased with shear rate increased (Chung *et al*, 1993).

These are two developing processes, gas separation with polymeric membranes and pervaporation. Gas separation with membranes is more developed technology than pervaporation. The membrane separation process produces a permeate enriched in the more permeable species and a residue enriched in the less permeable component.

In term of material development, membranes prepared from polyethersulfone (PES) have been received special attention for gas separation due to some of them possessing surprisingly high gas selectivities for gas pair  $O_2/N_2$  and  $CO_2/CH_4$ . Polyethersulfone also have many other desirable properties, such as spinnability, thermal and chemical stability and mechanical strength. These properties are essential to yield a membrane module with stable and predictable long-term performance.

## 1.2 Problem Statement

Most of gas separation membranes are the solution-diffusion type. The key of membrane performance variables are selectivity, permeability and durability. For solution-diffusion membranes permeability is defined as the product of the solubility and diffusivity. Traditionally, there has been a trade-off between selectivity and permeability; high selectivity membranes have more permeability and vice versa. Membrane based gas separation technology has some problems that must be solved before commercial use. For many gas separations, application membranes with high selectivity and permeability are not available.

One of the major problems confronting the use of membrane based gas separation processes in a wide range of application is the lack of membranes yielding high flux and high selectivity. Therefore, by using different of shear rate, were expected to enhance the membrane performance. These are the major study need to accomplish in this field to make the membrane capable in producing what we want without problem above.

### **1.3 Objectives of the Research**

1. To fabricate high selectivity and permeability asymmetric polyethersulfone (PES) membrane for gas separation.
2. Improving phase inversion condition to enhance membrane selectivity by controlling the shear rates used that affect the molecular orientation.
3. To study the effect of using different operating pressure on the gas separation performance.

### **1.4 Scopes of the Research**

1. Fabrication of polymer solution using PES, N-methyl-2-pyrrolidone (NMP) and water.
2. Characterized of the developed membrane using pure gases  $N_2$  and  $O_2$  as test gases.
3. Characterised the performance of using different operating pressure on separation of  $N_2$  and  $O_2$  gases.

## **CHAPTER II**

### **LITERATURE REVIEW**

#### **2.1 History of Membrane Based Separation**

Membrane based separation processes over the last three decades have proved their potential as better alternatives to traditional separation processes. Although report concerning the permeability of synthetic membranes date back to the mid 19<sup>th</sup> century, membrane science and technology study started as in early 15<sup>th</sup> century (Boretos, 1973).

An early demonstration of gas separation using natural rubber membranes date back to the 1830's. Gas separation using polymeric membranes has achieved important commercial success in some industrial processes since the first commercial scale membrane gas separation system was produced in the late 1970's. In order to extend its application and compete successfully with traditional gas separation, processes such as cryogenics, pressure swing adsorption and absorption and researchers made great attention in fabricating high separation performance membranes in both academia and industry (Wang *et al*, 2002).

The Table 2.1 provides the history of development of the membrane technology.

**Table 2.1 : Milestones in the development of membrane based separation**

<b>Name of Inventor</b>	<b>Year</b>	<b>Invention</b>
Abbe Nollet	1748	Wine and water were separated with animal skin by reverse osmosis
J.K. Mitchell	1831	First scientific observation related to gas separation
Thomas Graham	1850	Graham's Law of diffusion
L. Kahlenberg	1906	The separation of a mixture of a hydrocarbon and an alcohol through a rubber membrane
D. H. Hagerbaumer	1955	Conducted the first quantitative investigation with a microporous Vycor glass membrane with a high-pressure drop across it to allow for the separation of liquid-liquid mixtures.
Leob and Sourirajan	1961	Make the first anisotropic membrane
Binning et al	1965	Operation of separating a liquid-liquid mixture into a vapor mixture using a nonporous polymeric film.
Permea Inc.	1980	Launched its hydrogen separating Prism membrane
Gesellschaft fur Trenntechnik	1982	Installed a pervaporation plant to separate water from concentrated alcohol solutions.
Exxon	1990	Pervaporation in its refineries to separate hydrocarbon mixtures containing aromatics and aliphatics.



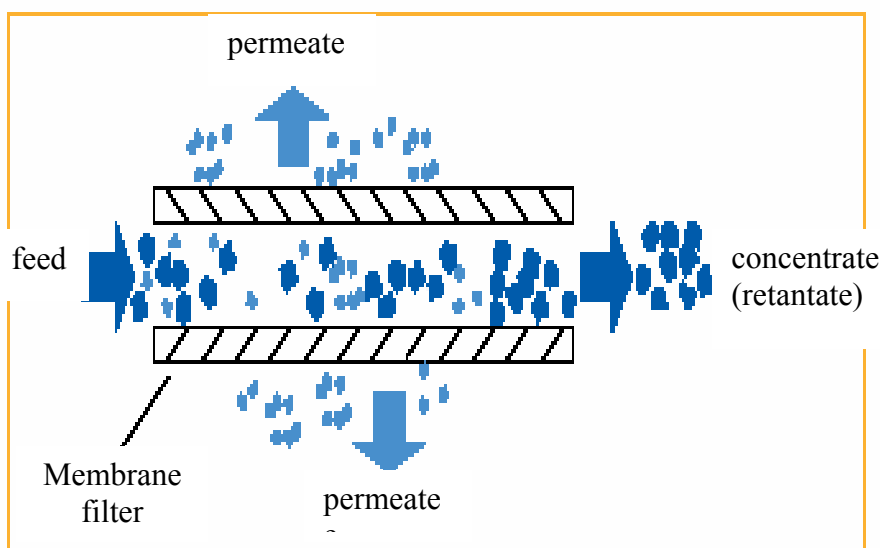
It was only in the last decade that the first mixed gas permeation experiments were conducted to evaluate the true separation property of membranes. Most of the models describing the mixed gas transport behavior are based on modifications to single gas transport models. Furthermore, these models only provide a description of the mixed gas transport phenomena under steady-state and simplified experimental conditions. The lack of experimental data hinders understanding of the true mixed gas transport phenomena through membranes. The modern era of gas separation membrane was introduced when polymeric membranes became economically viable. H<sub>2</sub>-recovery was the first major application of membrane gas-separation technology followed by the CO<sub>2</sub>/CH<sub>4</sub> separation and the production of N<sub>2</sub> from air (Pereira, 1999).

Since then, membrane-based gas separation has grown into a US\$ 150 million per year business and substantial growth in the near future is likely. Several research studies (Pereira, 1999; Di Luccio, 1994; Pinnau, 1994) have focused the membrane formation in order to control the properties of the resulting membrane and optimize the applications, compared to other developing membrane processes such as gas separation and pervaporation (Souza *et al*, 1998).

## **2.2 Overview of Membrane**

Membrane is a barrier that can separate the chosen component in liquid or solvent only that can pass through when giving pressure to it. Separation of membrane is a process that separates the particle by using the medium called membrane. The liquid will force to pass through the membrane by giving pressure. In separation membrane process, the component that is bigger in a solution will be block. From that, two phases will appear where one of them rich of the component or vice versa. (Geankoplis, 1980)

Membrane scientists continue to discuss the best way to classify membrane processes. As shown in Figure 2.1 feed through the membrane and molecules smaller than the cut off weight of the membrane pass through the membrane as permeate. Larger molecules, excluded by the membrane pores are retained as retentate (Estabrook, 2003).



**Figure 2.1:** Membrane Separation Process (Baker, 2002)

### 2.3 The Advantages of Membranes Technologies.

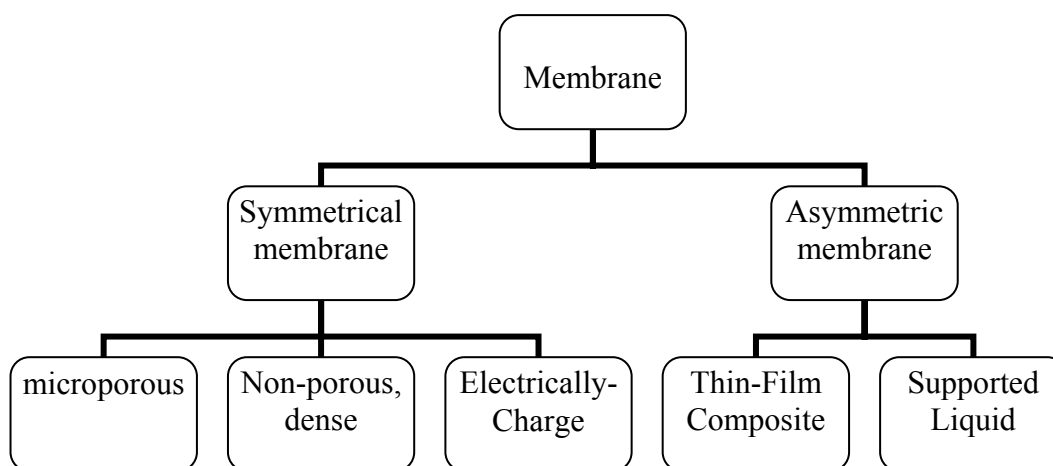
The technologies of membrane separation have been developing to be the top of process separation. The advantage of membranes separation has been found in certain processes such as producing, separation, recovering, and drying (Koros *et al*, 1998). The advantages are:

1. The membranes are highly selective and so it has high effectiveness in separation process.

2. Membrane processes are characterized by low energy consumption, possibility of different module design and easy scale up. These advantages make these processes superior to many other established separation processes.
3. The membrane based separation processes are costly effective and environmentally friendly.
4. These polymers not only exhibited better thermal and mechanical properties than natural polymers, but also presented a wide range of gas transport and separation properties.
5. Membrane process are able to recover minor but valuable components from a main stream without substantial costs.
6. The separation process of membrane do not used large or complex machine that have to more from a part of plant to another part of plant. It only consist some instrument that is easy to operate. This process can be continuously.

## 2.4 Classification of Membranes

Referring to figure 2.2, membrane can be classified into two types which is symmetrical membrane and asymmetric membrane.



**Figure 2.2:** Classification of Membrane (Baker, 2002)

### **2.4.1 Symmetrical Membranes**

Symmetrical membranes have a uniform composition structure throughout, and they can be porous or dense. The resistance to mass transfer in these membranes are determined by the total membranes thickness. A decrease in membrane thickness result in an increased permeation rate (Strathmann, 1980).

#### **2.4.1.1 Microporous Membranes**

The simplest form of microporous membrane is a polymer film with cylindrical pores or capillaries. However, more commonly microporous membranes have a more open and random structure with interconnected pores. They are very similar in structure and function to conventional filters. However in contrast with conventional filters, these pores are extremely small (Strathmann, 1980).

#### **2.4.1.2 Non-porous, Dense Membranes**

This type of membranes consists of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rates within the membrane, which are determined by their diffusivity and solubility in the membrane material. Thus, this type of membranes can separate permeants of similar size if their concentration in the membrane material differ significantly (Strathmann, 1980).

#### **2.4.1.3 Electrically-Charged Membranes**

These types of membranes are also referred to as ion-exchange membranes. They can be dense or microporous, but most commonly are very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. Separation is achieved

mainly by exclusion of ions of the same charge as the fixed ions on the membrane structure, and is affected by the charge and concentration of ions in the solution. This type of membranes is used for processing electrolyte solution in electrodialysis.

#### **2.4.2 Asymmetric Membranes**

Asymmetric membranes are used primarily for pressure driven membrane processes, such as ultrafiltration and gas separation. Their structure consist of a very thin (0.1 to 2.0 $\mu\text{m}$ ) polymer layer on highly porous 100 to 200 $\mu\text{m}$  thick sublayer (Strathmann, 1980). This means that this membrane consist two layer; a thin, dense and nonporous skin layer that perform the separation, supported by on a finely microporous substrate that made from the same material that only provides the mechanical strength (Baker, 2002). The sublayer only acts as a support and does not affect the separation characteristics or the permeation rate of the membrane in pressure driven processes. To obtain high permeation rates, the selective layer of gas separation membranes must be extremely thin (Baker, 2002). Since the permeation rate in ultrafiltration or gas separation processes is inversely proportional to the thickness of the thin barrier layer, asymmetric membranes exhibit much higher permeation rates than symmetric structures of comparable thickness. Another advantage of asymmetric membranes is the membranes are surface filters retaining all the rejected materials at the surface where they can be removed by shear forces applied by the feed solution moving parallel to the membrane surface (Costello I.M., 1994).

Ideal asymmetric membranes for gas separation should meet the following requirement. (Paul and Yampol, 1994)

1. The selective skin layer should defect free so that gas transport takes places exclusively by solution diffusion not by poorly selective flow through process
2. The selective layer should be as thin as possible to maximize the gas fluxes

3. The supporting substructure should not contribute any resistant to gas transport
4. The substructure should provide sufficient mechanical strength to support the delicate selective layer in high pressure operation.

#### **2.4.2.1 Thin-film Composite Membrane**

This membrane consist of a thin dense film of highly cross-linked polymer formed on the surface of a thicker microporous support. The dense polymer layer is extremely thin, on the order of 0.1 mm or less, so membrane permeability is high. Because it is highly cross-linked its selectivity is also high.

#### **2.4.2.2 Liquid Membranes**

Liquid membranes have become increasingly significant in the context of facilitated transport that utilizes carriers to selectively transport components such as metal ions at a relatively high rate across the membrane interface. Generally, formation of a thin film is not a problem. Difficulty is encountered, in maintaining and controlling this film and properties during a mass separation process (Lin W.H., 1999).

### **2.5 Applications of Membrane Separation Processes**

Seven major membrane processes were covered: four developed processes, microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and electrodialysis (ED) and one developing processes, gas separation with polymer membranes (Cussler, 1987).

The first three processes, microfiltration, ultrafiltration, and reverse osmosis are related filtration techniques, in which a solution containing dissolved suspended solutes

is forced through a membrane filter. The solvent passes through the membrane and the solutes are retained. These processes differ principally in the size of the particles separated by the membrane.

Microfiltration is considered to refer to membranes that have pore diameters from 1000 Å. Microfiltration membranes are used to filter suspended particulates, bacteria or large colloids from solution. Ultrafiltration refer to membranes having pore diameter in the range 20-1000 Å. Ultrafiltration membranes can be used to filter dissolved macromolecules such as proteins from solution. In the case of reverse osmosis, the membrane pores are so small in the range of 5-20 Å in diameter that they are within the range of the thermal motion of the polymer chains. Reverse osmosis membranes are used to separate dissolved microsolute such as salt from water. The principal application of reverse osmosis is the production of drinking water from brackish groundwater or the sea (Koros, 1998).

The fourth fully developed membrane process is electrodialysis, in which charged membranes are used to separate ions from aqueous solution under the driving force of an electrical potential difference. The process utilizes an electrodialysis stack, built on the filter-press principle and containing several hundred individual cells formed by a pair of anion and cation exchange membranes. The principal application of electrodialysis is the desalting of brackish groundwater (Riley, 2001).

Gas separation with membranes is the more mature of the two developing technologies. In gas separation, a mixed gas feed at an elevated pressure is passed across the surface of a membrane that is selectively permeable to one component of the feed. The membrane separation process produces a permeate enriched in the more permeable species and a residue enriched in the less permeable species. Current applications are the separation of hydrogen from argon, nitrogen and methane in ammonia plants, the production of nitrogen from air and the separation of carbon dioxide from methane in natural gas operation (Riley, 2001). Table 2.2 shown the detail of membrane separation process.

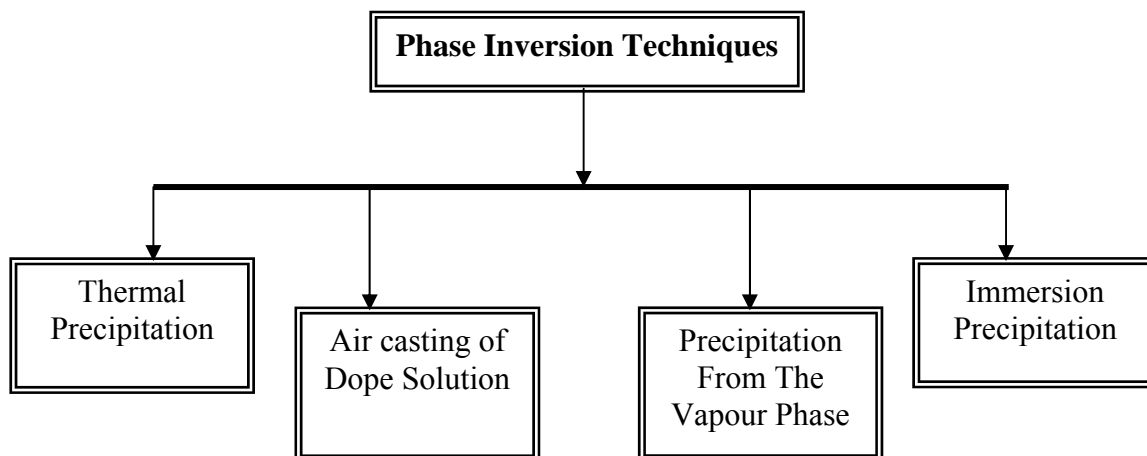
**Table 2.2:** Applications of Membrane Separation Process (Baker,2002)

<b>Separation Process</b>	<b>Por Size/ Nature Of Species Retained</b>	<b>Process Driving Force</b>	<b>Applications</b>
Microfiltration	0.02-10 $\mu\text{m}$	10-500 KPa	Sterile solution/water purification Beverage filtration effluents Cell harvesting
Ultrafiltration	10-200 Å	0.1-1 MPa	Dairy (whey recovery, precheese concentration) Electrocoat colloids Effluents (oil-water, pulp and paper, dye-stuffs, tannery) Biological (enzymes, fermentations) Water purification
Reverse Osmosis	1-10 Å	2-10 MPa	Water desalination, ultrapure water, dairy industry, effluent treatment (metal-finishing, photographic, chemical processes), biomedical applications, and pharmaceutical industries.
Electrodialysis	Cation & anion membrane	Electrical potential gradient	Water desalination, acidity reduction in citrus juice, deionization of whey
Gas Separation	Depend on gas size	1-10 bar	H <sub>2</sub> recovery/removal, CO <sub>2</sub> removal O <sub>2</sub> enrichment, helium recovery, N <sub>2</sub> enriched air, pollution control, sour gas treating,



## 2.6 Membranes Formation

In the membrane field, the term “phase inversion” is commonly used to describe the phase separation process. Membrane can be prepared by phase inversion techniques and can be categorized into four different techniques as shown in Figure 2.3.



**Figure 2.3:** Phase Inversion Techniques (Baker, 2002)

In the air casting technique process, the polymer is dissolved in a mixture of a volatile solvent and less volatile nonsolvent. During the evaporation of the solvent, the solubility of the polymer decreases and then phase separation takes place. In the precipitation from the vapor phase process, phase separation of the polymer solution is induced by penetration of nonsolvent vapor in the solution. For thermal induced phase separation (TIPS) technique, it is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying. In the immersion precipitation case, a polymer is cast as a thin film on a support or extruded through a die, and is subsequently immersed in a nonsolvent bath. Precipitation can occur because of the good solvent in the polymer solution is exchanged with nonsolvent in the coagulation bath (Fleming, 1998).

Among these techniques, immersion precipitation is widely used to produce commercial gas separation membranes and other membrane based-separation. Immersion precipitation technique is divided into three categories: wet phase inversion technique, dry phase inversion technique and dry/wet phase inversion technique.

### **2.6.1 Wet Phase Separation**

The wet phase separation technique is the most common method for preparation and production of polymeric membrane. A cast thin layer of a polymer solution is immersed in a liquid nonsolvent for polymer that is miscible with polymer solvent. The exchange of the solvent from thin layer of polymer solution with a nonsolvent from the coagulation bath produces thermodynamic instability in now ternary membrane forming system. The thermodynamic instability is resolved by the separation into polymer-rich phase forms a solid membrane matrix while the polymer-lean phase leaves a porous structure by leaching out the system (Nusa Vogrin *et al.*, 2002).

### **2.6.2 Dry Phase Separation**

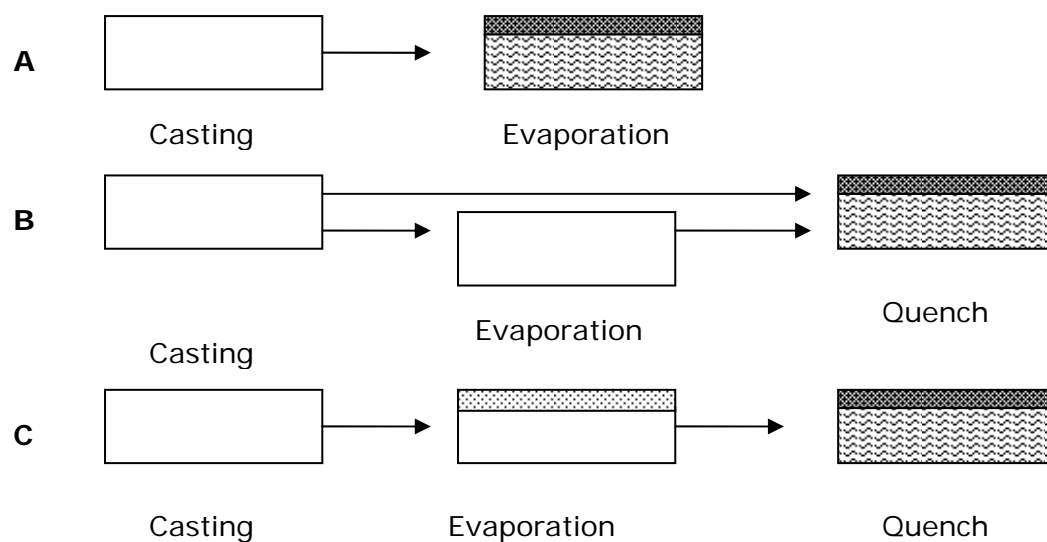
Flat sheet skinned asymmetric membrane are generally made by a casting solution consisting of polymer, solvents and non-solvent. If the non-solvent components are less volatile to the solvent components, evaporation will ultimately produce a critical non-solvent concentration that causes the membrane to be transform from a single phase to a two phase structure. If the solvents and non-solvents components are removed solely by evaporation, membrane formation is defined as a dry phase inversion process (Pinnau, 1991).

### **2.6.3 Dry / Wet Phase Inversion**

Asymmetric flat sheet polyethersulfone (PES) membrane can be prepared using a simple dry/wet phase inversion method. The flat sheet membrane was prepared by

casting a dope solution on a glass plate by using a pneumatically controlled casting machine with appropriate shear rate. The asymmetric membrane was then quenched immediately and smoothly in an aqueous bath at room temperature and remained there for two whole days for solvent-nonsolvent exchange process to occur. After that, the membrane was immersed in an alcohol nonsolvent bath for a day and then dried at room temperature for another day (Pinnau, 1991).

Comparisons between wet and dry processes are appropriate and can be discussed in terms as shown in Figure 2.4.

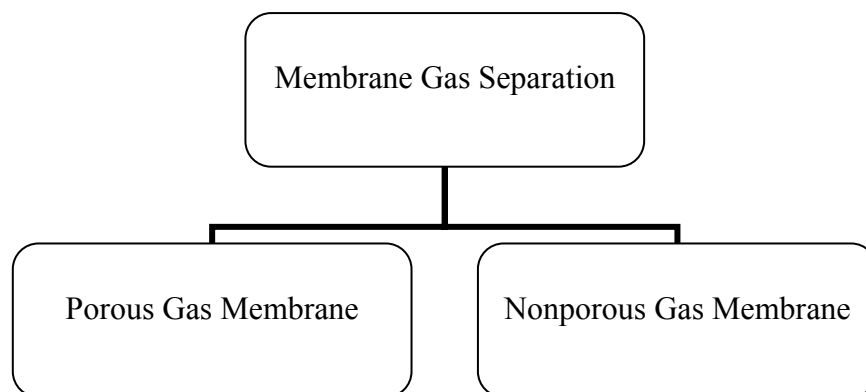


(A) dry phase inversion, (B) wet phase inversion, (C) dry/wet phase inversion

**Figure 2.4:** Schematic representation of phase inversion processes (Baker, 2002)

## 2.7 Fundamental of Gas Separation

The separation of gas can be divided into two ways which is through porous gas membrane and nonporous gas membrane.



**Figure 2.5:** Membrane Gas Separation

### 2.7.1 Gas Separation in Porous Membranes

The gases are separated because of the molecular size of small pores in the membrane. If the pores are relatively large, for example from 0.1 to 10  $\mu\text{m}$ , gases permeate the membrane by convective flow, no separation occurs in this case. If the membrane pores are extremely small, on the order of 5 Å to 20 Å, then molecular sieving separates the gases. However, transport through this type of membrane is complex and includes both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores (surface diffusion). If the pores are smaller than 0.1  $\mu\text{m}$ , then the pore diameter is the same size as or smaller than the mean free path of the gas molecules. In this case, diffusion through such pores is governed by Knudsen diffusion and the transport rate of any gas is inversely proportional to the square root of its molecular weight (Koros, 1998).

### 2.7.2 Gas Separation in Nonporous Membranes

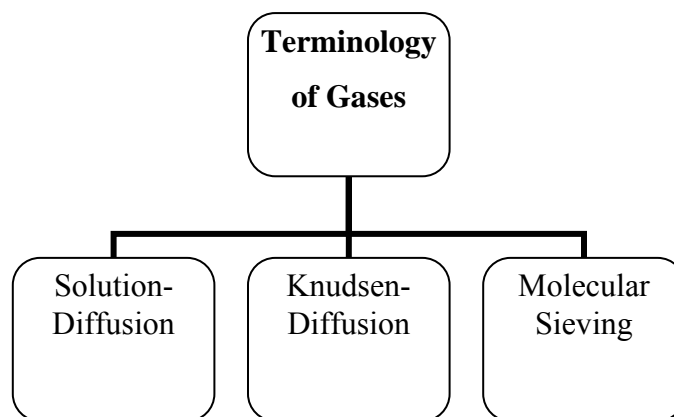
Solution-diffusion mode is the simplest description of gas transport in the nonporous dense membranes. In solution-diffusion mode, gas molecules from the upstream gas phase absorb into the membrane then diffuse across the membrane and finally desorbed on the down stream gas phase side. The membrane materials used in most separations are glassy polymers which derive their selectivity primarily from their ability to separate gases based on subtle differences in penetrant sizes (Wang, 2002).

**Table 2.3:** Lennard-Jones collision diameter of some gas molecules

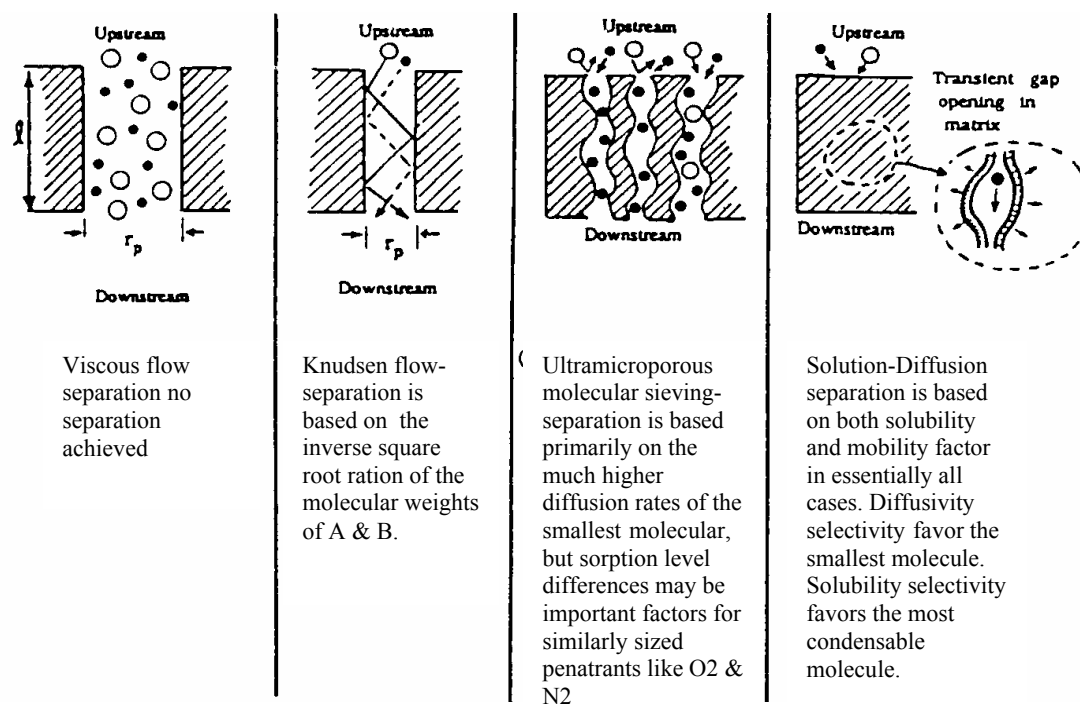
Gas molecules	Lennard-Jones Collision diameter (Å)
Helium	2.58
Hydrogen	2.92
Carbon Dioxide	3.30
Oxygen	3.43
Nitrogen	3.68
Methane	3.82

## 2.8 Terminology of Gases

The terminology of gases can be divided to 3 ways which is Solution-Diffusion, Knudsen-Diffusion, and Molecular Sieving.



**Figure 2.6:** Terminology of gases



**Figure 2.7:** Schematic representation of main mechanism of membrane-based gas separation (Baker, 2002)

As shown in figure 2.7, gas separation can be performed using membrane based on one of three general transport mechanism: which are Knudsen-diffusion, solution-diffusion and molecular sieving. Solution-diffusion through polymer selective layers is used exclusively in current commercial devices and will be discussed in detail in this review. Molecular sieving have received attention due to reported higher productivities and selectivities than solution-diffusion membrane. Fragility and fouling by condensibles have precluded the commercialization of large scale commercially robust systems based on either ultramicroporous carbon or glass hollow fiber membrane

The third type of separation, based on Knudsen diffusion, relief upon pores in the barrier layer that are smaller in diameter than the distance a molecule would travel in the gas phase between collisions to create a separation. For an equimolar feed, such as “Knudsen” diffusion process gives relative permeation rates equal to inverse square root of the molecular weights of the gases (W.J Koros and G.K Fleming, 1993)

## 2.9 Gas Permeation Experiment

Pure gas permeation tests were performed at 27°C and pressures at 1 atm. Pressure-normalized fluxes,  $(P/L)_i$  of nitrogen and oxygen permeating through a membrane were determined from bubble flow meter measurements as described by Pinnau:

To calculate the permeability we use the equation 2.1

$$\left(\frac{P}{L}\right)_i = \frac{Q}{\Delta P_i A} \quad \text{and} \quad Q = V/t \quad (2.1)$$

Where,

- Q represent of volumetric flow rate of gas at standard temperature and pressure ( $\text{cm}^3/\text{s}$ )
- $\Delta P$  is the trans membrane pressure difference (cm Hg)
- A represent the membrane surface area ( $\text{cm}^2$ )

To calculate the selectivity we use the equation 2.2

$$\alpha_{A/B}^* = \frac{(P/L)_A}{(P/L)_B} \quad (2.2)$$

Where,

- $\alpha_{A/B}$  is define as the pure gas pressure-normalized permeation rate ratio of gas A to gas B.

From the above equation, it is evident that the permeance of a membrane depends on the thickness of the effective separation layer while the selectivity is independent of the dense layer thickness (Chung et al, 1999).

## 2.10 Current Status of Gas Separation Membranes

Membranes offer lower energy cost and viable economics at low volume, simplicity of operation, portability, compactness and mechanical reliability. Polyethersulfone membrane-based separation, for example have grown to represent about one-third of new liquid-nitrogen production capacity for small users. Membrane separations are not as competitive for large units or where high purity is required. Most of today gas separation membranes are formed into hollow-fiber modules due to their low production cost. Currently only eight or nine polymer materials have been used to make at least 90% of the total installed gas separation membrane-based systems.



Table 2.4 show the principal gas separation markets, producers and membrane systems (Koros, 1991).

**Table 2.4:** Principal Gas Separation Markets, Producers and Membrane Systems

<b>Company</b>	<b>Markets</b>	<b>Membrane Material Used</b>	<b>Module Type</b>
Permea	Large gas companies	Polysulfone	Hollow fiber
Medal(Air Liquide)	Nitrogen separation	Polyimide / polyaramide	Hollow fiber
IMS (Praxair)	Hydrogen separation	Polyimide	Hollow fiber
Grace Membrane System (GMS)	CO <sub>2</sub> , H <sub>2</sub> and natural gas separations	Tetrabromo polycarbonate	Spiral wound
Separex	CO <sub>2</sub> , H <sub>2</sub> and methane	Cellulose acetate	Spiral wound
Ube Industries	CO <sub>2</sub> and vapor recovery	Polyimide	Hollow fiber
GKSS Licensees	H <sub>2</sub>	Silicone rubber	Plate frame
Cynara (Natco)	CO <sub>2</sub>	Cellulose acetate	Hollow fiber
Membrane Technology and Research	Dehydration	Silicone rubber	Spiral wound

## **2.11 Factor Affecting Gas Permeation in Membrane**

### **2.11.1 Pressure**

When the dilute solutions pass through the membrane, the fluxes will increase, but after the optimum pressure the purity of the fluxes become low because the pressure will destroy the membrane structure of the membrane. So the particle that larger than the membrane pores also can pass through the membrane.

### **2.11.2 Temperature**

Flux increases proportionally with temperature due to reduce kinematics viscosity. Increased flux leads to an increased rate of fouling. Also temperature increases the chemical activity and foulant deformation, which can accelerate foulant layer densification, resulting an increased hydraulic resistance. Ultimately, flux in a fouling system is reduced at a higher rate from a temperature increase, and may actually stabilize at a lower value than would occur at lower temperatures.

### **2.11.3 Flow Rate**

For every different concentration, when the flow rate of process is increase, the diffusion through the membrane will totally increase. Thus, the fluxes will also increase.

### **2.11.4 Concentration**

The increasing of solute concentration when operating time it will cause the polar increase, thus the effects of fluxes will decrease.

## **2.12 Effect of Shear Rate**

The effect of shear rate molecular orientation has been observed in the separation performance of ultrafiltration, reverse osmosis and gas separation membranes. The selectivity increased with increasing dope extrusion rate in flat sheet membrane while the gas permeation rate reduced. The relative selectivities also increased with shear rate increase. Once a certain shear is reached, all permeances increase, while their selectivities decrease with an increase in shear rate (Chung *et al*, 1993).

The molecular orientation in the active layer of PES membranes was in increase in molecular orientation in the high sheared membranes which enhance the gas selectivity. Membrane forming polymer solutions are typically shear thinning and exhibit viscoelastic properties (Ismail *et al*, 2003).

Rheological conditions during manufacture would also affect membrane performance by altering molecular orientation. According to the result, using polarized reflection infrared spectroscopy and gas permeation test, molecular orientation was found to be intensified in the high-shear membrane pressure-normalized flux and selectivity as well as raising the selectivity if the membrane, some even surpass the recognized intrinsic selectivity of the membrane polymer (Shilton et al, 2002). Shear rate is calculated by the following equation:

$$\text{Shear Rate} = v/g \quad (2.3)$$

and

$$v = s/t \quad (2.4)$$

where,

- $v$  = velocity of coasting knife
- $g$  = gap setting
- $s$  = distance of bubble
- $t$  = time (constant)